

Multi-Atom Resonant Photoemission Revisited

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INTRODUCTION

In recent work at the ALS, it has been suggested that a new type of interatomic resonant photoemission effect exists, and that this effect furthermore has the potential of providing a new probe of near-neighbor atomic identities, bonding, and magnetism [1]. The phenomenon has been termed multi-atom resonant photoemission (MARPE). In measuring this effect, the photoelectron intensity of a given core level from atom "A" (e.g. O 1s from MnO) is monitored while the photon energy is tuned through a strong absorption edge for a core level on another atom "B" in the sample (e.g. the Mn 2p edges in MnO). Initial observations on MnO and other metal oxides showed significant positive interatomic resonant effects in photoemission of up to 100% [1]. Additional measurements in Auger emission and soft x-ray emission from MnO seemed to confirm that such effects were also present in secondary decay processes as a result of resonant enhancement of the initial O 1s core hole formation [2]. A theoretical model for these effects based on the extension of intraatomic resonant photoemission ideas to the interatomic case was also developed and compared favorably with experiment [3]. Other measurements on transition-metal compounds [4] and an adsorbate-substrate system [5a] seemed to confirm these measurements and analysis.

Subsequently, it has been realized that such experimental measurements require very careful allowance for potential detector non-linearities [5b,6,7], since the observed electron intensities (particularly inelastically scattered backgrounds) change dramatically in going over any core resonance. In particular, the common detector used for the first measurements [1,4,5a], the standard microchannel plate-plus-CCD camera incorporated in the Gammatdata-Scienta series of electron spectrometers, exhibits not only a typical saturation effect for high countrates, but also a quadratic component of counting that goes above linear for low countrates. Thus, spectra obtained in this low-countrate regime, while not exhibiting any kind of saturation effect, can be artificially enhanced in intensity in passing over a core-level resonance. We here report the results of measurements which are fully corrected for these detector non-linearities. These data reveal the correct form of the MARPE effects for MnO, which are in turn compared with the results of two theoretical models for the effect: a microscopic quantum-mechanical approach and a macroscopic x-ray optical or dielectric approach. We also comment on other recent measurements in which such interatomic effects have been studied. Further details and discussion appear elsewhere [6, 7].

EXPERIMENTAL PROCEDURE AND RESULTS

The measurements were performed on beamline 4.0.2, but with prior data obtained at beamline 9.3.2 also being reanalyzed via a detector response function measured on 4.0.2. A Gammatdata-Scienta ES200 spectrometer was used to measure all spectra, with its multichannel detector system being operated in the greyscale (or analogue) mode, as set up by the manufacturer. The

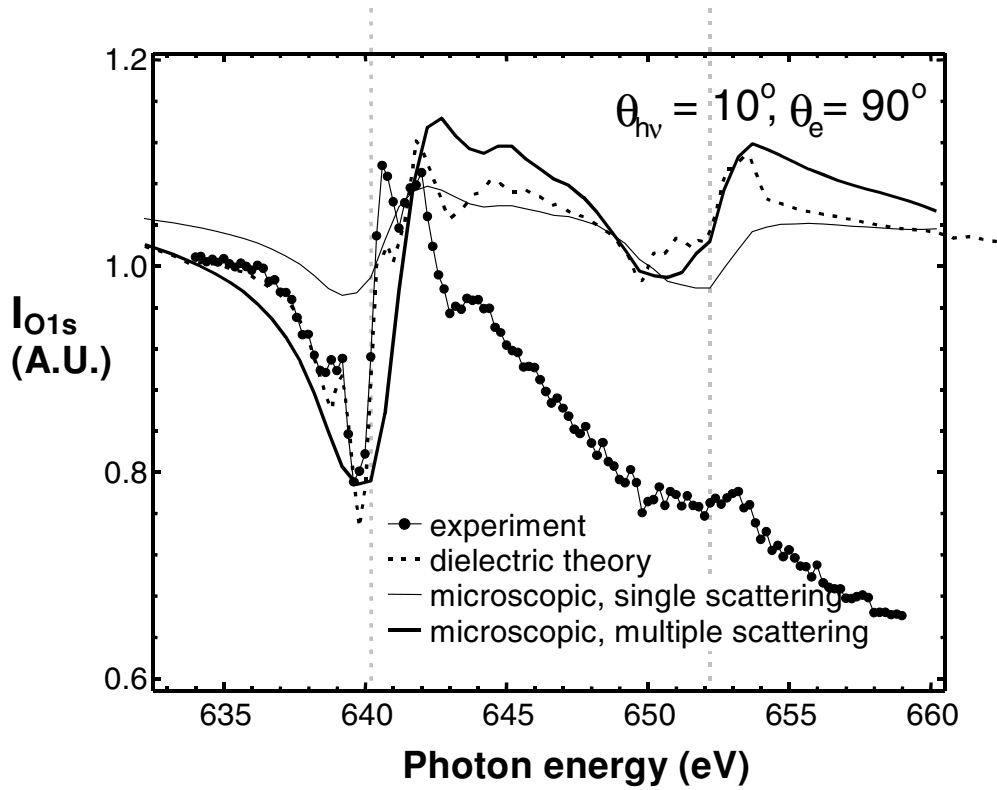


Figure 1. Corrected O 1s intensity from MnO(001), after correction for detector non-linearity, as a function of photon energy and for x-ray incidence angle = $\theta_{hv} = 10^\circ$, electron exit angle = $\theta_e = 90^\circ$ (normal to surface): experimental data (connected points) are compared to theoretical curves calculated using a second order microscopic many-body theory corresponding to single radiation scattering (thin solid line), an infinite-order microscopic theory corresponding to multiple radiation scattering (thick solid line), and an x-ray optical dielectric theory based on experimental optical constants δ and β (dashed curve). The overall slope in experiment from ~ 1.0 to 0.63 is simply a photoelectron diffraction effect [6,7], with the resonant effects for Mn $2p_{3/2}$ and $2p_{1/2}$ riding on top of this.

sample was MnO(001), with the surface being cleaned by an established recipe of ion bombardment and annealing *in situ* [1,2].

The detector response function was first measured by using a standard x-ray tube source and varying its excitation current at fixed high voltage. An initial quadratic component riding on the linear component was found at low countrates, with quantitative details described elsewhere [5b, 6, 7]. This detector response function was then used in a point-by-point fashion to correct intensities in O 1s spectra obtained as the photon energy was scanned over the Mn $2p_{3/2}$ and $2p_{1/2}$ absorption edges in MnO. Results for an x-ray incidence angle of 10° with respect to the surface are shown in Figure 1. The form of both resonances is seen to be a decrease and then an increase in intensity as a given absorption threshold is approached from lower energy, rather than a steady increase as observed previously [1]. Similar O 1s data have been found for other incidence angles on MnO, with a strong dependence on this angle [6,7].

THEORETICAL MODELING AND DISCUSSION

A microscopic model for these effects incorporating all relevant many-electron interactions has been developed [3,7] and it has also been shown that this, under certain conditions appropriate for photoelectron emission from a homogeneous sample with a flat surface, can be reduced to a model involving the detailed x-ray optical interactions with a dielectric medium. The results of calculations based on both models are compared with experiment in Figure 1. Microscopic

theory agrees well with experiment, provided that interactions beyond the usual second-order Kramers-Heisenberg form are included, with these corresponding to multiple scattering of the incoming radiation on resonance. The microscopic theory will be necessary for describing systems with enhanced near-neighbor electron correlation effects and/or with nanometer-scale heterogeneity, as well as for free molecules [7]. Macroscopic theory based upon experimental optical constants agrees excellently with experiment, and points out that such effects will be more pronounced for grazing angles of x-ray incidence.

Other groups have by now observed similar effects to those in Figure 1 for CuO [8], for a molecule adsorbed on a metallic surface [9], and in the angular distributions from a polyatomic free molecule [10]. These results also appear to require the microscopic model for their interpretation. Previously observed MARPE effects in soft x-ray emission [2] were also affected by the same detector non-linearity, but once taken with a linearized detection system show effects expected on the basis of the dielectric model [2b, 11]; however, effects beyond this model of up to 3-5% are also possible in the data so far presented.

CONCLUSIONS

Multi-atom resonant photoemission as now viewed via fully corrected data and expanded theory thus still represents a newly-discovered aspect of the photoemission process that should provide a unique probe of near-neighbor identities, bonding, and magnetism in systems with enhanced many-electron interactions and/or with nanometer-scale heterogeneity, as well as in free molecules.

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